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(54) **Flame resistant materials**

(57) A combustion modified material comprises a polymer foam incorporating expandable graphite in which a substantially water-insoluble neutralising substance is incorporated to control the pH value of the material during and after manufacture.

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Improvements in or relating to normally flammable
materials rendered flame-resistant

The invention relates to improvements to combustion modified materials, particularly but not exclusively, plastic materials.

The term "combustion modified materials" as used herein refers to all those normally flammable organic polymeric materials which are in the form of foam material and which are capable of being mixed with expandable graphite to render the material more flame-resistant.

The combustion modified materials to which the invention relates includes foams made from synthetic or natural polymer materials such as elastomers, polystyrene, polyurethane, polyalkenes, eg polyethylene, polybutylene, polypropylene, and mixtures of such materials.

The use of expandable graphite for reducing the flammability of polyurethane foams is known from UK Patent No 2,168,706. This patent discloses the incorporation of expandable intercalated graphite into foam material, particularly polyurethane foam of whatever form, including rigid foams.

A particular difficulty of using expandable graphite in polymeric materials arises from residual acid which remains in the flakes of expandable graphite even after repeated washing. Over a period, ranging from days to years, the acid diffuses to the surface and makes the graphite measurably acidic (eg 5g of the graphite flakes suspended in 25cm^3 of water will exhibit a pH of 2 or less after 1 minute at room temperature).

This amount of acidity gives rise to serious problems in use of the graphite, for example in polyurethane foams.

Firstly the low pH due to the expandable graphite inhibits reaction between the poly-isocyanate and polyol and the foam fails to rise adequately or cross-link fully. A further problem arises from the low pH solubilising certain impurities (eg transition metals) commonly found in natural graphites and which interfere with production of a strong, resilient foam or the required characteristics of other combustion modified flammable materials.

Finally, continued evolution of acid over a period of several years in service risks long-term damage to combustion modified material or in the case of upholstery foams, the fabric coverings over the foam, metal components embedded in the foam, etc.

A known and partially-effective solution to the acidity problem in polyurethane foams is incorporation of neutralising alkalis into the foam-forming mixture of expandable graphite, polyol, poly-isocyanate, etc. Selection of alkalis requires great care, however, as many produce harmful effects during the material-forming process or in the final product. In the case of foams the foam-forming process is rendered unsatisfactory. US Patent No 3,579,644 discloses the addition of ammonium hydroxide to expandable graphite to overcome the problems of the instability of a wide range of materials incorporating expandable graphite. In the case of foam materials which include expandable graphite, some inhibition of foaming and impairment of the product was evident when ammonium hydroxide was used as a neutralising substance.

When using such alkalis a particular problem arises from the continuing acid evolution from the expandable graphite grains. If just sufficient alkali is added to neutralise the acid shortly after manufacture of the expandable graphite, continuing acid evolution may reduce the pH to

unacceptable levels either before the graphite grains are used or during subsequent service. On the other hand, addition of larger amounts of alkali (sufficient to ensure the long-term absence of acidity) leads to high initial pH which itself leads to problems, for example, in the manufacture of polyurethane foam it inhibits the foam-forming reaction.

The invention is concerned with improving combustion modified flammable material which contains expandable graphite by reducing the deleterious effect of acid and by reducing the problem of high pH generation while not interfering with the proper formation of the material.

A further object of the invention is to produce a long-lasting effect of neutralising low pH generation in finished flammable materials which neutralising effect can continue for a long period after they have been put into use.

Accordingly the invention provides a combustion modified material as hereinbefore defined, which includes expandable graphite mixed with a substantially water-insoluble acid neutralising substance selected from the group of such substances which generate a pH value of less than 10 when made into a 10% (w/w) mixture with water.

The preferred combustion modified materials are flexible polymer foams, the particularly preferred materials being polyurethanes.

Preferably the acid neutralising substance generates a pH value of between 4 and 9 when mixed with constituents of the flammable material and the expandable graphite.

The acid neutralising substances used in this invention are substantially insoluble in water, so that they can be relied upon to remain in situ in the combustion modified material, neutralising acid as it is released from the graphite.

Calcium carbonate is a preferred neutralising substance. A 10% suspension of calcium carbonate in water gives a pH value of approximately 9.8. However, acid-susceptible silicates (eg wollastonite) are alternatives.

Under the same condition as for calcium carbonate, wollastonite provides a pH value 9.6.

Water-insoluble members of other families of substances including borates, phosphates, and salts of organic acids, can have a similar effect of remaining in situ to modify the acid evolution effect of incorporating expandable graphite into the combustion modified materials.

Metal powders, for example, zinc, certain oxides such as zinc oxide, zeolites or other silicates capable of ion exchange, for example, in the calcium exchange form and ion exchange resins, may also be used as the acid neutralising substance. Mixtures of acid-neutralising substances may be used.

In a preferred aspect of the invention there is provided a combustion modified polyurethane foam comprising a polyurethane foam containing expandable graphite mixed with a substantially water-insoluble acid-neutralising substance selected from the group of such substances which generate a pH value of less than 10 when made into a 10% mixture with water.

Preferably, the acid-neutralising substance is pre-mixed with the graphite before adding a mixture of the two to the foam-making ingredients. This will allow neutralisation of any acid already on the surface of the graphite grains before it can adversely affect the organic components. This pre-mixing also improves the likelihood of early neutralisation of acid released after foam-making.

It is further preferred that the acid-neutralising substance be present as a coating on the expandable graphite grains and/or be contained within pores or

crevices within the grains. Either would encourage interception and neutralisation of the acid before it was able to harm the polymeric constituents.

According to another aspect of the invention a method of manufacture of a combustion modified flammable material (as hereinbefore defined) comprises the steps of incorporating into the material to be modified 5-50% by weight of expandable graphite and between 0.1% and 50% by weight (based on the weight of graphite) of a substantially water-insoluble acid-neutralising substance selected from the group of such substances which generate a pH value of less than 10 when made into a 10% mixture with water.

The invention will now be particularly described, by way of example only, by means of the following examples, examples 5 to 8 being included for comparison purposes.

EXAMPLE 1

Manufacture of expandable graphite

A natural flake graphite, (80% retained on 50 mesh sieve) was oxidised in concentrated sulphuric acid, washed and dried to make it expandable.

An aqueous suspension of 5g of this freshly-made expandable graphite in 25cm³ of water gave a pH of 2.0 (ie low enough to make it unsuitable for use in foams - see example 5).

Manufacture of acid suppressed fire retardant

1 Kg batches of this material were mixed respectively with 20, 50, 67 and 100g of fine precipitated calcium carbonate by dry blending.

The pH was measured of 5g samples of each mixture in 25cm³ of water (room temperature; 1 minute after preparation). pH measurements were made in this way both from freshly-made graphite calcium carbonate mixtures and from mixtures that had been allowed to stand for 2 weeks. The following results were obtained:

Weight of Expandable <u>Graphite</u>	Weight of Calcium <u>Carbonate</u>	pH of Freshly- <u>made mix</u>	pH after <u>2 weeks</u>
1000g	20g	4	4
1000g	30g	5	5
1000g	67g	5	5
1000g	100g	6	6

The addition of calcium carbonate had therefore stabilised the pH within acceptable limits.

25g of each of these expandable graphite/calcium carbonate mixtures were added to 75g (total weight) batches of a proprietary mixture for making resilient polyurethane foam (poly-isocyanate, polyol-surfactant, blowing-agent and catalyst). In each case, within one minute the mixture began to rise and after 10 minutes it had formed a well-set, strong (but flexible) low-density foam, with good fire-retardant behaviour.

EXAMPLE 2

Example 1 was repeated but, in this case, 1 Kg of the expandable graphite was intimately mixed with 50g of fine precipitated calcium carbonate suspended in 5000cm³ of water, the solids filtered off and dried. Immediately after manufacturing, a suspension of 5g of the graphite/calcium carbonate mix in 25cm³ of water gave a pH of 5.5 after 1 minute. 25% of this mixture was added to a proprietary mixture for making flexible polyurethane foam (poly-isocyanate, polyol, surfactant, blowing agent and catalyst). Within 1 minute the mixture began to rise and after 10 minutes it had formed a well-set, strong (but resilient) low-density foam, with good fire-retardant behaviour.

EXAMPLE 3

Example 2 was repeated but using 200g of fine wollastonite (calcium silicate) in place of the calcium carbonate. An aqueous suspension of this mixture gave a pH of 5.7. 25% of this mixture, when incorporated in a polyurethane foaming mix, did not inhibit either rise or setting of the foam.

EXAMPLE 4

100g of expandable graphite, as made in Example 1, was dispersed in 1000cm³ of water in which 5g of calcium hydroxide had been suspended. Carbon dioxide gas was bubbled through the suspension until all the calcium hydroxide had been turned into calcium carbonate. The solids were filtered off and dried to give a mixture of expandable graphite particles and calcium carbonate in which a significant proportion of the calcium carbonate coated the surfaces of graphite particles or was lodged within crevices in the particles.

The pH of a suspension of this mixture was 5.5. The mixture performed satisfactorily as a fire-retardant additive for polyurethane foam.

EXAMPLE 5

Aqueous suspensions of the unmodified expandable graphite, immediately after its manufacture, were found to have a pH of 2.0. After standing for 4 weeks this had decreased to 1.2. In both instances the acidity was too high for production of satisfactory polyurethane foams, with both rise and setting being inhibited.

EXAMPLE 6

250g of expandable graphite was added to 1000cm³ of water containing 1.85g of calcium hydroxide (some dissolved and the remainder in suspension). The solids were filtered-off and dried to give a mixture consisting of approximately 99.4% expandable graphite and 0.6% calcium hydroxide. Immediately after preparation, a suspension of this mixture had a pH of 2.5 and the material behaved reasonably well as an additive for polyurethane foams.

However, after standing for 4 weeks, it gave suspensions with a pH of 2.0 and was sufficiently acidic to seriously retard both the rise and setting of polyurethane foam.

EXAMPLE 7

Example 6 was repeated but the quantity of calcium hydroxide was increased to 3.5g in order to ensure the absence of excessive acidity after standing for 4 weeks. Immediately after preparation, however, the mixture gave suspensions with a pH of 11 and this excessive short-term alkalinity interfered with production of polyurethane foam.

Examples 6 and 7 together show that calcium hydroxide is unsuitable for use in this invention.

EXAMPLE 8

250g of expandable graphite was washed with 1000cm³ of 1% ammonium hydroxide solution for 5 minutes, filtered-off and dried. Immediately after preparation, the pH of an aqueous suspension was 4. When added to polyurethane foaming mixes, some inhibition of both rise and setting was evident.

After standing for 4 weeks, the graphite gave an aqueous suspension of pH 3.2 and was found to seriously inhibit foam formation. Ammonium hydroxide is thus also unsuitable for use in this invention.

CLAIMS

1. A combustion modified material (as hereinbefore defined) which includes expandable graphite mixed with a substantially water-insoluble acid neutralising substance selected from the group of such substances which generate a pH value of less than 10 when made into a 10% (w/w) mixture with water.
2. A combustion modified material according to claim 1 in which the acid neutralising substance is selected from calcium carbonate, acid-susceptible silicates, borates, phosphates, salts of organic acids, metal powders, metal oxides, zeolites and ion exchange resins, and mixtures thereof.
3. A combustion modified material according to claim 1 or 2 which is flexible polymer foam.
4. A combustion modified material according to claim 1, 2 or 3 which is a polyurethane foam.

5. A combustion modified material according to claim 1, 2, 3 or 4 in which the amount of expandable graphite is in the range 5 to 50 per cent by weight based on the total weight of combustion modified material, and the amount of acid neutralising substance is in the range 0.1 to 50 parts by weight per hundred parts by weight of expandable graphite.
6. A combustion modified material according to claim 4 in which the pH value of a mixture of the constituents of the polyurethane foam with the expandable graphite and the acid neutralising substance is in the range 4 to 9.
7. A combustion modified material according to any one of claims 4 to 6 in which the acid neutralising substance is calcium carbonate or wollastonite.
8. A method for the manufacture of a combustion modified material (as hereinbefore defined) which comprises the steps of incorporating into the material to be modified 5 to 50 per cent by weight of expandable graphite and between 0.1 and 50 per cent by weight (based on the weight of graphite) of a substantially water-insoluble acid neutralising substance selected from the group of such substances which generate a pH value of less than 10 when made into a 10% mixture with water.

9. A method according to claim 8 in which the expandable graphite and the acid neutralising substance are mixed before adding them to the material to be modified.
10. A method according to claim 9 in which the acid neutralising substance is a coating on and/or is contained within pores or crevices within grains of the expandable graphite before the latter is added to the material to be modified.
11. A method according to claim 9 or 10 in which, in the manufacture of combustion modified polyurethane foam, a mixture of expandable graphite and acid neutralising substance is incorporated into the foam by adding the mixture to the foam making ingredients before the foam is formed.
12. A combustion modified material according to claim 1 substantially as described in any one of the foregoing Examples 1 to 4.